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# Spectrophotometric Determination of $Hg^{2+}$ after Solid Phase Extraction on Microcrystalline Naphthalene

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## ABSTRACT

Mercury is quantitatively retained with 1, 5-diphenylcarbazone (DPC) on microcrystalline naphthalene in the pH range 6.5-8.5 from a large volume of aqueous solutions of various samples. After filtration, the solid mass consisting of the mercury complex and naphthalene was dissolved in 5.0 mL of dimethylformamide (DMF) and mercury was determined by spectrophotometric method at 542 nm against the reagent blank. The linear calibration range for mercury was 30-1800 μg L-1 in DMF solution with a detection limit of 20 μg L-1. The relative standard deviation for eight replicate measurements of 1.0 μg of mercury in 5.0 mL of DMF was 2.5%. The effect of potential interfering ions was investigated and the proposed method was applied to the determination of mercury in water samples.

**Keywords:** Mercury determination; Preconcentration; Spectrophotometry; 1, 5- Diphenylcarbazone; Microcrystalline Naphthalene

## INTRODUCTION

Mercury is one of the most toxic heavy metals. Elemental and inorganic mercury are found in scientific instruments, electrical equipment, dental amalgams, felt making, disinfectants and enters the environment as metallic, inorganic and organic mercury compounds through various industries like pulp and paper industry, chlor-alkali plants, gold and silver mining, electrical industry, paints, fungicides and pharmaceuticals [1].

The toxicity of mercury depends on its chemical species and it is found that organomercurials are more toxic than inorganic mercury compounds. Mercury and its compounds are reported to be mutagenic and teratogenic in nature [2].

The correlation between clinical symptoms and whole blood mercury depends both on the mercury species and or the duration of exposure. Whole-blood mercury levels are the best measure of recent inorganic mercury and elemental mercury vapor absorption. Normal blood levels of mercury do not exceed 1–3 μg dL−1. Hair analysis indicates past exposure, and the mercury blood to hair ratio is ~2/250 [3]. The determination of total mercury in solution is usually carried out by spectrophotometric methods [4, 5], atomic absorption-emission spectrophotometry [6-9], inductivity coupled plasma mass spectrometry [10-11], atomic fluorescence spectrometry [12] and voltametric method [13]. However, due to the presence of mercury in environmental samples

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at low levels, its separation from other elements present and also the use of a pre-concentration step prior to Hg determination is usually necessary.

The solid-phase extraction (SPE) techniques make it possible to extract the components of interest in the aqueous samples with minimal usage of organic solvents. In SPE methods, the aqueous sample solution first passes through a cartridge or a tube containing an adsorbent that retains the analytes of interest.

Then the analytes are eluted from the adsorbent using a minimal amount of a suitable solvent. The major disadvantage of the SPE cartridge and tubes is the tendency for fine particulates to plug the first holding the adsorbent in the place. However, the use of the flat disks with high cross-sectional area (SPE disks) may largely prevent this problem. The decreased back pressure encountered with the SPE disks makes much higher flow rates possible, and their wide bed decrease the chance of plugging. In recent years, the SPE disks have been utilized for the extraction and determination of many different organic and environmental matrices [14-18]. Moreover, the SPE cartridges and disks modified by suitable ligands are successfully used for the separation and sensitive determination of metal ions [19-21].

In this paper, a highly selective and sensitive preconcentration method has been developed for spectrophotometric determination of mercury by using 1, 5-diphenhylcarbazone modified naphthalene as adsorbent. Various parameters affecting the method were evaluated and the validity of the procedure was tested by recovery experiments.

## EXPERIMENTAL

### Apparatus and reagents

A Shimadzu UV 160A spectrophotometer with a 1.0 cm quartz cell was used for absorbance measurement at a fixed wavelength. A Metrohm pH meter model 692 was employed for pH measurements. All glasswares were washed with a mixture of concentrated sulphuric and nitric acid (1:1) before use.

All the reagents were of analytical reagent grade and were used without further purification. The standard stock solution of mercury (II) (1000 mg L-1) was prepared by dissolving 0.1708 g of Hg(NO3)2.H2O (Merck) in water in a 100 mL volumetric flask. Working solutions were prepared by appropriate dilution of the stock solution with water.

A 0.01% solution of 1, 5-diphenylcarbazone (DPC) was prepared by dissolving 0.01 g of DPC in 100 mL of 95% ethanol. Buffer solutions of pH 3-6 and 6-10 were prepared by mixing appropriate ratios of a 0.50 M acetic acid and 0.50 mol L-1 sodium acetate solution and 0.10 mol L-1 sodium dihydrogen phosphate solution and 0.10 mol L-1 dipotassium hydrogen phosphate solution, respectively. A 20% solution (w/v) of naphthalene was prepared by dissolving 20.0 g of naphthalene in acetone in a 100 mL volumetric flask.

### General procedure

An aliquot of mercury solution (containing 0.15 – 9.0 μg of Hg) was placed in a conical flask fitted with a ground-glass stopper. The pH was adjusted to ca. 7.0 with 2.5 mL of the buffer solution. The solution was diluted to 50 mL with water, and 1.8 mL of 0.01% DPC was added. The solution was mixed well and allowed to stand for one minute, then 1.4 mL of 20% solution of naphthalene in acetone was added with continuous shaking. The solid mass formed, consisting of naphthalene and the metal complex was separated by filtration on a Whatman filter paper (No. 1041). The residue was washed with water and then sucked dry. The solid mass was dissolved in dimethylformamide (DMF) and made up to volume with the same solvent in a 5 mL volumetric flask. The residual water was removed by addition of 0.3 g of anhydrous sodium sulphate. The absorbance of the colored complex was measured at 542 nm against the reagent blank.

## RESULTE AND DISCUSSION

Mercury forms a stable colored complex with DPC. The absorption spectrum of the complex formed has an absorption maximum at 542 nm against reagent blank.

### Reaction conditions

The effect of pH on recovery of mercury was examined and the results are shown in Figure 1.

The adsorption of mercury complex on the microcrystalline naphthalene was found to be maximal in the pH range 6.5-8.5. In subsequent studies, the pH was maintained at ca. 7.0. Variation of the volume of the buffer added between 0.50 and 5.0 mL did not affect the retention of mercury and the use of 2.5 mL was chosen.

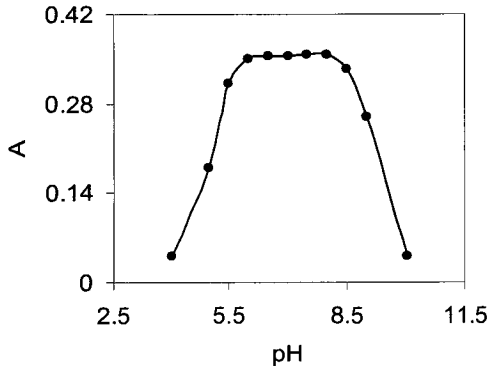


**Fig. 1.** Effect of pH on the adsorption of mercury.

The effect of concentration of DPC on the recovery of mercury was investigated by various amounts of 0.01% alcoholic solution of DPC. Mercury was quantitatively adsorbed on the adsorbent over the range 1.0-3.0 mL of the reagent. Therefore, 1.8 mL of the reagent was selected for subsequent experiments. In order to adsorb the mercury-DPC complex quantitatively, the amount of naphthalene must be chosen carefully. Various amounts of naphthalene (20% solution of naphthalene in acetone) were added to the sample solutions, keeping other variables constant. It was observed that the band height remained constant with the addition of 1.0-2.0 mL of 20% naphthalene solution. Therefore, 1.4 mL of 20% naphthalene solution was used in subsequent studies.

The experimental results indicated that distribution of the complex between the solid and liquid phases tends to be at equilibrium after shaking for 2.5 minutes.

The volume of the aqueous phase was varied in the range 10-500 mL under the optimum conditions, keeping the other variables constant. It was observed that the signal band was almost constant up to 240 mL (preconcentration factor of 48). However, for convenience, all the experiments were carried out with 50 mL of aqueous phase.

A number of solvents were examined to dissolve the metal complex along with the naphthalene. Since the solid mass was dissolved in a small volume of solvent, it is essential to select a solvent in which the chelate is highly soluble, and also allows sensitive UV-visible spectrophotometric measurements.

The solid material was soluble and stable in dimethylsulfoxide, DMF and ethyl acetate but was either not soluble or decomposed in chloroform, n-hexane, isoamyl alcohol and dioxane. DMF was chosen because the complex gave the highest apparent molar absorptivity at 542 nm. It was found that 4 mL of this solvent was sufficient to dissolve the complex and naphthalene.

It was found that the surplus water in the final solution caused the absorbance to decrease by 10-12 % and led to an error in the determination. Thus, it was necessary to eliminate the water attached to naphthalene, by addition of anhydrous sodium sulfate prior to measurement.

## Calibration, sensitivity and precision

The calibration graph for the determination of mercury was prepared according to the general batch procedure under the optimum conditions developed above (Fig 2). The detection limit (signal-to-noise ratio = 3) was 20 μg L-1 for mercury in the optimum conditions. Calibration linearity was maintained in the range of 30–1800 μg L-1 mercury with a correlation coefficient of 0.9995 and relative standard deviation of □ 2.5% for 1.0 μg mercury in 5.0 mL of DMF (n = 8).

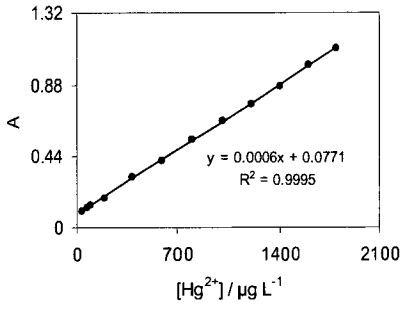


**Fig. 2.** Calibration curve; pH = 7.5, 1.4 mL of 20 % naphthalene in acetone, 40 mL of aqueous phase, 20 mL 0.01 % alcoholic DPC solution and 5.0 ml of DMF as solvent.

### Interference of foreign ions

Various salts and metal ions were added to a sample solution containing 4.0 μg of mercury and the general batch procedure was applied. The tolerance limit was set as concentration required to cause □ 3% error in the determination of mercury. The results obtained are given in Table 1. Among the anions examined, large amounts of fluoride, chloride, bromide, nitrate, acetate and sulphate could be tolerated, but thiosulphate and thiocyanate were seriously interfered. Among the metal ions studied, many of them did not interfere. The interference from Al(III) and Fe(III) can be masked by addition of 3.0 mL of 5% NaF solution. Moreover, the interference from Cu (II) can be masked by addition of 5.0 mL of 1 % of glycine solution. Thus, the proposed method can be applied for determination of mercury in water samples.

## APPLICATION

The method was applied for the determination of mercury in well,river and tap water samples. The river water sample was filtered through a Millipore 0.45 μm pore-size membrane into previously cleaned polyethylene bottles and was analyzed within 6 h of collection.

The reliability of the method was checked either by spiking the sample or comparing with data obtained by cold vapor atomic absorption spectrometry (CVAAS). As shown in Table 2, the recovery of spiked sample is good and there is satisfactory agreement between the results and data obtained by CVAAS.

## CONCLUSION

The method described in this paper allows rapid, precise and reliable determination of mercury in aqueous solutions. The main advantages of the present procedure are the enhanced sensitivity of the spectrophotometric method, rejection of matrix constituents, low cost, fairly easy operation and fast analysis. Table 3 shows the comparison of the present method and some other reported spectrophotometric methods.

## ACKNOWLEDGEMENT

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**Table 1.** Effect of foreign ions on the determination of mercury

| Ion | Mole ratio |
|---|---|
| $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ | 1000 |
| $Co^{2+}$ | 800 |
| $Pb^{2+}$ | 500 |
| $Zn^{2+}$ | 240 |
| $Al^{3+}$ | 150[a] |
| $Fe^{3+}$ | 100[a] |
| $Cu^{2+}$ | 60[b] |
| $Cd^{2+}$ | 18 |
| $Ni^{2+}$, $Ag^+$ | 12 |
| $CH_3CO_2^-$, $PO_4^{3-}$, $SO_4^{2-}$, | 1000 |
| $NO_3^-$, $F^-$, $Cl^-$, $Br^-$ | 1000 |
| $I^-$ | 500 |
| $ClO_4^-$, $C_2O_4^{2-}$ | 400 |
| $S_2O_3^{2-}$ | 10 |
| $SCN^-$ | 5 |

aAfter masking with 3 mL of 5 % NaF solution
bAfter masking with 5 mL of 1 % glycine solution

**Table 2.** Determination of mercury in water samples

| Samples | Mercury (μg $L^{-1}$) | | CVAAS | Beer's law range(μg $L^{-1}$) | Remarks |
|---|---|---|---|---|---|
| Recovery (%) | Added | found* | | | |
| Well water 1 | - | < LD | < LD | < LD | - |
| | 200 | 203 ± 4.5 | 204 ± 3.9 | 204 | 101 |
| Well water 2 | - | < LD | < LD | < LD | - |
| | 200 | 196 ± 4.9 | 203 ± 3.4 | 203 | 98 |
| Tap water 1 | - | < LD | < LD | < LD | - |
| | 200 | 202 ± 4.3 | 201 ± 2.9 | 201 | 101 |
| Tap water 2 | - | < LD | < LD | < LD | - |
| | 200 | 201 ± 3.8 | 198 ± 3.2 | 198 | 101 |
| Polluted river water | - | 45 ± 1.2 | 48 ± 1.0 | 48 | - |
| | 200 | 242 ± 5.2 | 250 ± 4. | 250 | 99 |

*Average of six determination ±standard deviation

**Table 3.** Comparison with other spectrophotometric methods

| S No Reagents/Ref | Medium/pH | $\lambda_{max}$ | Beer's law range(μg $L^{-1}$) | Remarks |
|---|---|---|---|---|
| (1) Cadion-2B [22] | 8.5-9.8 pH | 524 | 100-1200 | Sensitive but interference from $Cu^{2+}$, $Pb^{2+}$, $Ni^{2+}$, $Zn^{2+}$ |
| (2) Rhodamine-B [23] | Acidic | 558 | 100-1000 | Sensitive but interference from $Cd^{2+}$, $Zn^{2+}$, $Fe^{3+}$, $Mg^{2+}$ |
| C P DA[a] [24] | Alkaline | 540 | 80–800 | More sensitive, selective and free from interference of $Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$ |
| (4) Present method | 6.5-8.5 pH | 542 | 30-1800 | More sensitive but interference from $Cd^{2+}$, $Ni^{2+}$, $Ag^+$ |

a: o-carboxy phenyl diazoamino p-azobenzene

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